

**CALIBRATION OF THE EU OXYBAROMETER FOR NAKHLITES.** J. Makishima<sup>1</sup>, G. McKay<sup>2</sup>, L. Le<sup>3</sup>, M. Miyamoto<sup>1</sup> and T. Mikouchi<sup>1</sup>. <sup>1</sup>Department of Earth and Planetary Science, Graduate school of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan, makki@eps.s.u-tokyo.ac.jp, <sup>2</sup>Mail Code SR, NASA Johnson Space Center, Houston, TX 77058, USA, <sup>3</sup>ESC Group, Jacobs Sverdrup, Houston, TX 77258, USA.

**Introduction:** Martian meteorites have various characteristics, which are direct clues to understanding the petrogenesis of Mars rocks. The variation in oxidation state among the Martian meteorites must have important implications for redox conditions of the Martian crust/mantle and overall differentiation on Mars. Wadhwa [1] and Herd et al. [2] reported that Martian basalts were formed under a range of oxidation states, suggesting complex petrogenesis processes. The nakhlites, which have rather different characteristics from basaltic shergottites, may give us additional clues to Martian petrogenesis.

The oxidation states of meteorites are usually described by the oxygen fugacity ( $fO_2$ ) under which the meteorites crystallized. One of the methods to estimate the oxygen fugacity is the depth of Eu anomaly.  $Eu^{2+}/Eu^{3+}$  is determined by the oxygen fugacity and partitioning is different for  $Eu^{2+}$  and  $Eu^{3+}$ . Therefore, the depth of Eu anomaly in a mineral is a function of the oxygen fugacity and the  $Eu^{2+}/Eu^{3+}$  in the melt from which the mineral crystallized. This method has some advantages over another major method, the two-oxide oxybarometer [3], which can more easily be affected by subsolidus processes. The Eu oxybarometer can analyze the cores of the earliest formed crystals in Martian meteorites, which means it can give us a better indication of the oxygen fugacity of the parent melt. The calibration of the Eu oxybarometer has been done with the basaltic shergottites before [4]. However, it has never been applied to nakhlites (Oe et al. [5] measured the depth of Eu anomaly in the synthetic pyroxene only at QFM).

Partition coefficients are strongly affected by phase compositions, especially pyroxene Ca content and melt Al content [e.g., 5,6]. The composition of nakhlite pyroxene is rather different from basaltic shergottite pyroxene. Thus, there may be problems in applying the Eu oxybarometer calibration for the basaltic shergottites [7] to nakhlites. Thus, we report in this abstract preliminary results of our experimental calibration of the depth of Eu anomaly in pyroxene vs. oxygen fugacity for nakhlites.

**Experimental Methods:** Starting material consisted of glass powders of the NJ4 composition that our group has studied previously [8,9]. This composition was doped with 1.0 wt%  $SrCO_3$ , 0.7

wt%  $Sm_2O_3$ , 1.0 wt%  $Eu_2O_3$  and 0.7 wt%  $Gd_2O_3$ . ~125mg pellets of these mixtures were put on Pt loops and homogenized in CO-CO<sub>2</sub> gas mixing DelTec furnaces at 1300 °C for 48 hours, and then quenched. Homogenized charges were placed back into the furnaces slightly below the liquidus and held at constant temperature or cooled down at 0.5 °C/hr to various temperatures, growing pyroxene crystals. Oxygen fugacities of experiments were IW, IW+1.5, and QFM (IW+3.5). We analyzed quenched charges with the Cameca SX-100 Electron Microprobe at JSC using carefully selected background positions. We also reanalyzed charges from [5] under the same conditions.

**Results and Discussion:** To date we have had 3 successful experiments. Experimental conditions for these are shown in Table 1, and pyroxene compositions are compared with Nakhla pyroxene cores in Fig. 1. There is general agreement between experimental pyroxene compositions and Nakhla pyroxene core compositions.

Expt.	Oxygen fugacity	Start cooling	Quench temperature	Cooling rate
817	IW	1155°C	1150°C	0.5°C/h
818	IW+1.5	1155°C	1150°C	0.5°C/h
819	QFM	1159°C	1152°C	0.5°C/h

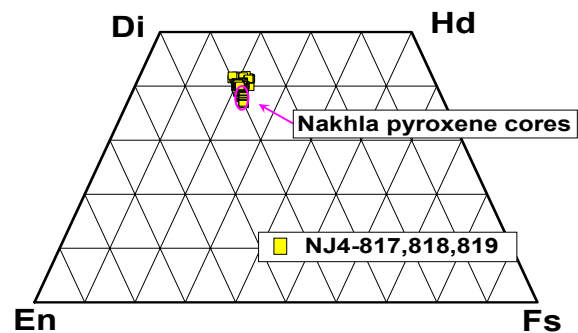


Fig. 1 Pyroxene compositions of our experiments (NJ4-817, 818, 819) and Nakhla pyroxene cores. We can see the general agreement between both pyroxene compositions.

Fig. 2 compares our REE partition coefficients with those of Oe et al. [10] (D values of Sr, Sm, Eu and Gd are redetermined in this study). For reasons that are not yet clear, our D values are slightly higher

than those of Oe's, and further experiments will be required to investigate these discrepancies. However, the charges run under more reducing conditions (NJ4-817, 818) have deeper Eu anomaly than one run under more oxidizing conditions (NJ4-819), as expected.

Fig. 3 shows our calibration of D(Eu/Gd) and D(Eu/Sm) in pyroxene vs. oxygen fugacity for our nakhlite experiments. In our result the D(Eu)/D(Gd) and D(Eu)/D(Sm) have somewhat different trends. We regard D(Eu)/D(Gd) as more reliable because we doped Eu and Gd together in one charge in our experiments, whereas we added Sm separately. Thus, Eu and Gd were more similarly affected by vagaries of crystallization than Sm. Moreover, [7] conducted similar experiments to ours, using synthetic shergottite melt compositions, and our trend for D(Eu/Gd) is similar to theirs. Consequently, we will use our D(Eu)/D(Gd) calibration to estimate the oxygen fugacity of the nakhlite parent melt.

Table 2 shows a comparison of D(Eu)/D(Gd) values from this study and our redetermined value from charges of [10] (redetermined is within 5% of original). It also shows D(Eu)/D(Gd) values for the nakhlite melt calculated from bulk rock and augite core analyses of [11,12]. The D ratio of Nakhla melt is between that of NJ4-817 (IW) and NJ4-818 (IW+1.5). Uncertainties in experimental values are from standard deviations of the mean of individual analyses, while uncertainty in the Nakhla value is a seat-of-the-pants estimate.

**Conclusions:** Results in Table 2 suggest that Nakhla formed under fairly reducing conditions. However, the slopes of the calibration curves in Fig. 3 are shallow, and this result is heavily dependent on (1) accurate determination of the partition coefficients, and (2) accurate estimation of Eu/Gd in Nakhla melt and pyroxene. High precision Eu, Gd, and Sm analyses of bulk nakhlite samples and nakhlite core pyroxenes are required to more definitively estimate the oxygen fugacity under which these samples crystallized. In addition, we need to conduct further experiments to confirm experimental reproducibility, especially considering the ~20% differences in D values between our experiments and Oe's [10]. Moreover, we need to determine the sensitivity of the calibration to melt Al content, because there is some ambiguity in the appropriate Al content of the nakhlite parent melt. This can have important effects on partition coefficients, as our group noted previously [10], but its effect on partition coefficient ratios used in the calibration is not yet known.

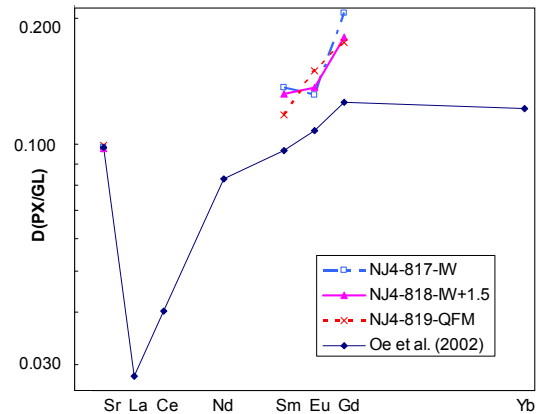


Fig. 2 REE and Sr pyroxene/liquid partition coefficients. Oe et al. values are from [10] (D values of Sr, Sm, Eu and Gd are redetermined). Our D values for Sm, Eu and Gd, are ~20% higher than those of [10] although we do not know the reason. Note the difference of the depth of the Eu anomalies between of NJ4-817 & 818 and NJ4-819. Charges under more reduced condition have deeper Eu anomalies.

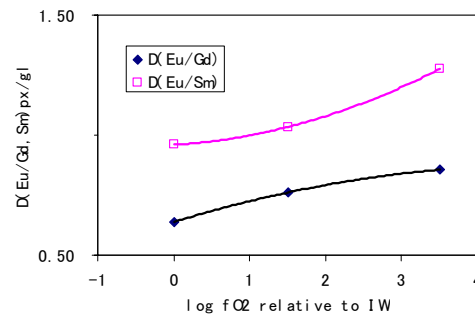


Fig. 3 Calibration of D(Eu/Gd)(pyroxene/glass) and D(Eu/Sm) (pyroxene/glass) versus oxygen fugacities (in log units relative to the IW buffer).

Table. 2 Pyroxene D(Eu)/D(Gd)			
Expt	fO <sub>2</sub>	D(experiment)	D(Nakhla)
817	IW	0.64±.002	0.7±0.1
818	IW+1.5	0.76±0.02	
819	QFM	0.86±0.04	
Oe	QFM	0.86±0.03	

**References:** [1] Wadhwa M. (2001) *Science*, 291, 1527-1530. [2] Herd C. et al. (2002) *GCA*, 66, 2025-2036. [3] McKay G. (2004) *Oxygen in the terrestrial planets*, 3036. [4] Wadhwa M. et al. (1994) *GCA*, 58, 4213-4229. [5] Oe K. et al. (2001) *LPSXXXII*, Abstract #2174. [6] McKay et al. (1986) *GCA*, 50, 927-937. [7] McCanta M. and Rutherford M. (2004) *Oxygen in the terrestrial planets*, 3028. [8] McKay G. et al. (1994) *LPSXXV*, 883-884. [9] Kaneda K. et al. (1998) *LPSXXXIX*, 1620-1621. [10] Oe K. et al. (2002) *LPSXXXIII*, 2065-2066. [11] Nakamura N. et al (1982) *GCA*, 46, 1555-1573. [12] Wadhwa M. et al (2004) *Antarct. Meteorite Res.*, 17, 97-116.